Journal of Hazardous Materials 300 (2015) 322–328

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

A zero-liquid-discharge scheme for vanadium extraction process by electrodialysis-based technology

Meng Wang[a,b,*], Hong-bo Xing[a,b], Yu-xiang Jia[a,b], Qing-chun Ren[c]

[a] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, China
[b] College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China
[c] Beijing Unisplendour Empyreal Environmental Engineering Technology Co. Ltd., Beijing 100083, China

HIGHLIGHTS

- A zero discharge scheme for vanadiumextraction process is proposed.
- The water transport in the electrodialysis process is analyzed quantitatively.
- The influence of concentration ratio in the electrodialysis process is explored.

ARTICLE INFO

Article history:
Received 15 November 2014
Received in revised form 19 May 2015
Accepted 25 May 2015
Available online 27 May 2015

Keywords:
Vanadium extraction
Zero-liquid-discharge
Industrial saline water
Water transport
Concentration ratio

ABSTRACT

The sharp increase of demand for vanadium makes the treatment of the wastewater generated from its extraction process become an urgent problem. In this study, a hybrid process coupling the electrodialysis with the cooling crystallization is put forward for upgrading the conventional vanadium extraction process to zero discharge. Accordingly, the objective of this work lies in evaluating the feasibility of the proposed scheme on the basis of a systematic study on the influences of membrane types and operating parameters on the electrodilysis performance. The results indicate that the relative importance of osmosis and electro-osmosis to overall water transport is closely related to the applied current density. The increase in the applied current density and the decrease in the mole ratio of water and salt flux will contribute to the concentration degree. Moreover, it is worth noting that a relatively large concentration ratio can result in the remarkable decrease of current efficiency and increase of energy consumption. In general, the reclamation scheme can easily achieve the recovered water with relatively low salt content and the highly concentrated Na_2SO_4 solution (e.g., 300 g/L) for producing high-purity sodium sulphate crystals.

1. Introduction

As one of the important chemical elements, vanadium is closely related with daily life and industrial production. Up till now, approximately 85% vanadium produced is used as an additive for improving steels besides some other applications, such as catalyzing the relevant chemical reactions and making ceramics and glass [1]. However, it is noteworthy that the potential application of vanadium in energy storage system will result in another big demand in the future [2]. At present, one of the important vanadium sources is the extraction from iron ore slag as a useful by-product, especially in China, Russia and South Africa. Unfortunately, a large quantity of wastewater with high salinity was simultaneously produced. Obviously, whether from environmental protection or resource reuse points of views, an effective scheme for the reclamation of the industrial saline water is urgently needed.

Nowadays, the treatment for concentrated salt effluents from various industries has attracted many interests whether from academic or practical points of view. For examples, different possibilities have been reviewed to treat or to discharge wastewater with high salinity [3–5]. Among them, the ED-based technology was paid special attention because of its unique advantages, such as the high water recovery, the reuse of salt and the low requirements for pretreatment. According to the public reports, there are mainly two electrodialysis-based approaches. One is the bipolar membrane electrodialysis (BMED) process, which can achieve acid

* Corresponding author at: College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China. Tel.: +86 532 6678 6513; fax: +86 532 6678 6513.
E-mail address: wangmeng@ouc.edu.cn (M. Wang).

http://dx.doi.org/10.1016/j.jhazmat.2015.05.042
0304-3894/

Table 1
The main properties of the membranes used in the ED process.[a]

Membrane type	Thickness (dry, mm)	Ion-exchange capacity (dry, mol/kg)	Area resistance (Ω cm^2)	Water content (%)	Transport number
Heterogeneous CEM	0.42 ± 0.04	2.0	11	35–50	>0.90
Heterogeneous AEM	0.42 ± 0.04	1.8	12	30–45	>0.89
CMV	0.13–0.15	–	2.0–3.5	–	>0.96
AMV	0.11–0.15	–	1.5–3.0	–	>0.96

[a] The data are collected from the product brochure provided by the manufacture.

and base as well as desalted water through water splitting and the oriented transport of ions. However, the BMED reclamation scheme for industrial effluent with high salinity still remain in laboratory research or pilot demonstration without successful industrial implementation because of some unsolved practical problems, for examples, relatively high cost of the bipolar membrane and relatively low ability of anion exchange membrane and cation exchange membrane to blocking acid and base. The other is conventional ED process with the desalination-concentration dual-purpose, which usually is coupled with other operations, such as evaporation and electrolysis [6–7]. In view of the maturity of equipment and technology, ED may be preferred for the treatment of concentrated salt effluents. However, some concomitant phenomena, such as the back diffusion of ions and the water transport between the dilute and the concentrate compartments, frequently deteriorate the technological process. For example, Jiang et al. tried to concentrate brine from RO plant by ED and concluded that water transport should be mainly attributed to electro-migration of the hydrated ions [7]. Galama et al. investigated the suitability of ED for seawater desalination and observed that the transported amount of electro-osmotic water is proportional to the applied current density, and the water transport embraces a significant effect on the concentration of the concentrate stream [8].

In this study, an industrial effluent from vanadium extraction process which is characterized as high salt content (e.g., 10–15% Na_2SO_4) comes into notice. In view of the significant change of Na_2SO_4 solubility with temperature, a hybrid process coupling the conventional ED with cooling crystallization is designed for reclaiming the industrial effluent. However, due to the strong affinity of SO_4^{2-} to H_2O molecules [9] (i.e., Gibbs free energies of SO_4^{2-} hydration, −1000 kJ/mol, is higher than that of Cl^-, −317 kJ/mol.), the achievement of highly concentrated stream may be slowed down or even prevented. Moreover, for an ED process with the desalination-concentration dual-purpose, a relatively large concentration difference must induce the oriented diffusion of ions and water. Accordingly, the objective of this work lies in evaluating the feasibility of the proposed scheme on the basis of a systematic study on the influences of operating parameters and membrane types on the water transport, including the osmosis and the electro-osmosis, current efficiency and energy consumption in the ED process. Hopefully, this study may help to expand applications of an ED-based reclamation scheme.

Table 2
Water quality of the saline effluent investigated in this study.

Items	Units	Values
V	mg/l	≤50
Cr	mg/l	≤0.5
Na^+	mg/l	about 23,000
NH_4^+	mg/l	25
SO_4^{2-}	mg/l	about 70,500
Fe^{3+}	mg/l	0.03
K^+	mg/l	350
Cl^-	mg/l	300
Si^{2+}	mg/l	13.9
Mg^{2+}	mg/l	0.03
Al^{3+}	mg/l	0.25
pH	–	7–9

2. Experimental

2.1. Experimental equipment

The membrane stack used in this work consists of twenty cell pairs, i.e., twenty AEMs and twenty-one CEMs are assembled in total. Considering the availability of commercial membranes and investment cost, the domestic heterogeneous membrane combination (products of Shanghai Shang-hua water treatment material Co. Ltd., China) is mainly used. Moreover, a CMV/AMV homogeneous membrane combination (products of the ASAHI GLASS Co. Ltd., Japan) is also attempted in the concentration process of the industrial effluent for comparison. All their main properties can be found in Table 1. The stack is equipped with polypropylene spacer with a dimension of 28 cm (length) × 16 cm (width) × 0.75 cm (thickness), in which the polypropylene turbulence accelerating mesh net is embedded. During the ED experiments, a desired fixed electrical voltage or current is supplied by a variable power source (0–64 V, 0–20 A, TPR series, Long-wei instruments Co. LTD., H.K.) by means of a couple of electrodes made of titanium coated with ruthenium with aid of 0.5 mol/L Na_2SO_4 solution used as electrode rinsing solution. Three plastic magnetic pumps (MP15R, Shang-hai Magnetic Pump Co. Ltd., China.) are employed to drive flows into stack. The flow rates are monitored by specified flow meters (LZBF-25, Tian-jin Wu-huan Instrument Factory, China).

2.2. Experimental procedures

In this work, the water sample was collected from the neutralization tank of a certain factory for vanadium extraction located in He-bei Province (China), into which the industrial effluent was directly discharged for the subsequent pH adjustment after the

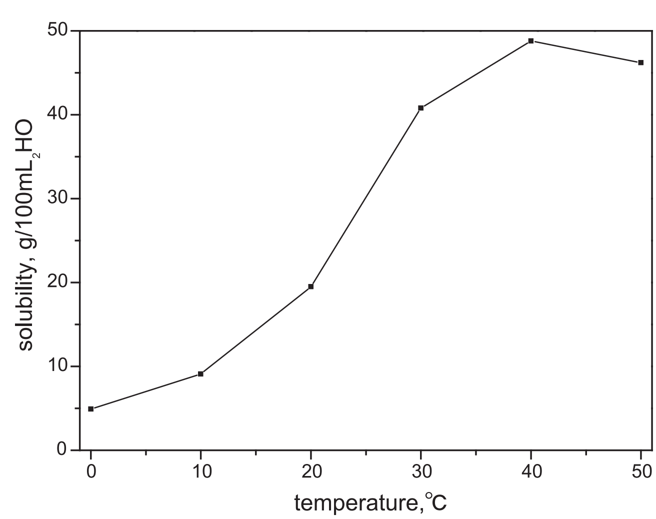

Fig. 1. The changes of the solubility of Na_2SO_4 with temperature.